AMENDED SPECIFICATION

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PATENT SPECIFICATION

868,463

DRAWINGS ATTACHED

868,463

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International Classification:—C08f, B29d, H01j.

COMPLETE SPECIFICATION

Improvements in Polymers

We, MINNESOTA MINING AND MANUFACTURING COMPANY, of 900 Bush Avenue, Saint Paul 6, Minnesota, United States of America, a Corporation organized under the laws of the State of Delaware, United States of America, do hereby declare the invention for which we pray that a Patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to adhesive tapes. More specifically the invention is concerned with the provision of adhesive tapes having backings in the form of films of an initially passive hydrogen-free fluorocarbon polymer.

Films and other articles of polytetrafluoroethylene normally possess passive surfaces which are both oleophobic and hydrophobic, and to which organic adhesives do not strongly adhere. Methods of activating these normally passive surfaces have been developed in which the surface is at least partially defluorinated by controlled reaction with suitable reactants. For example, brief contact with metallic sodium applied in solution in liquid ammonia, followed by washing with water, has been shown to provide on the surface of thin transparent polytetrafluoroethylene film a dark coloured opaque layer to which organic adhesives readily adhere but which greatly reduces the surface resistivity of the film.

In accordance with the invention adhesive tapes are produced by activating a surface of a backing in the form of a film of a passive hydrogen - free fluorocarbon polymer by irradiating it with ultra - violet radiation of wave lengths less than 2000 Angstroms in the presence of at least trace amounts of oxygen and applying an organic adhesive to the activated surface.

The exact nature of the resulting active surface, and the specific action occuring at the initially passive fluorocarbon surface, are not now fully understood but it is found that the transparency and high surface resistivity of the film backings of the tapes of the invention are preserved. No subsequent washing or other treatment of the backing is required before the organic adhesive is applied, and so firmly bonded to the backing is the adhesive that the tapes are capable of being unwound from roll form without delamination.

Electrical discharge has previously been used to remove residual vapours and the like from glass, metal and other surfaces in preparing components of evacuated systems for high vacuum experimentation. In such cases, the thus cleaned surfaces must be carefully preserved from subsequent contact with air, water vapor or the like. In the present system, the treated fluorocarbon polymer film remains surface - activated during prolonged exposure to the air as well as on washing with various aqueous solutions and organic solvents. Hence there appears to be involved much more than a mere cleaning of the surface.

Irradiation and other treatment of various plastic films to provide improved surface wetting with adhesives, inks, and other coatings has also been practiced. Thus, polyethylene films have been flame-treated, or exposed to electrical discharges, or treated with ozone, as a means of improving their receptivity for printing inks and the like. The action has

been said to involve dehydrogenation of the polymer, the formation of double bonds, and partial oxidation. The passive fluorocarbon film surfaces here to be treated need contain no hydrogen, and the fluorine - carbon bond is not ordinarily considered as being susceptible of oxidation; hence the type of treatment applicable to polyethylene would be expected to have no effect whatever on, for example, polytetrafluoroethylene. While such polymers may include hydrogen - containing catalyst fragments, the amount is so small that they may properly be designated as "hydrogen-free".

The invention will now be further described with reference to the accompanying drawings which illustrate a number of forms of apparatus in which the normally passive and non-reactive surfaces of the fluorocarbon film backings may be rendered perseveringly receptive of organic adhesives for the production of adhesive tapes in accordance with the invention.

In the drawings:

Figure 1 indicates in section a discharge chamber as applied to the treatment of polytetrafluoroethylene and similar backing films;

Figure 2 is a sectional view of the discharge chamber of Figure 1 taken along the line 2—2;

Figure 3 is a view in elevation of another form of apparatus, partly cut away to show interior detail;

Figure 4 represents in section a continuous treatment type apparatus;

Figure 5 is a plan view of the apparatus of Figure 4 with the upper electrode assembly removed;

Figure 6 represents a further form of treatment chamber, shown in section;

Figure 7 is a view of the apparatus of Figure 6 sectioned at the line 7—7;

Figure 8 schematically represents in section a commercial form of continuous treating apparatus; and

Figures 9 and 10 represent schematically two forms of apparatus as employed in the surface treatment of fluorocarbon backing films under atmospheric pressure.

The apparatus of Figures 1 and 2 includes a section 10 of heavy glass tubing, in this case having a length of about 3.5 inches and an internal diameter of 4 inches, fitted with metal bottom and top elements 11 and 12 which form a tight seal against the ends of the glass tube through ring gaskets 13 and 14. The member 11 is fitted with an outlet 15 connected to a suitable vacuum pump, and an inlet 16 fitted with a needle valve 17 for permitting re-entry of air to the evacuated chamber.

The bottom and top members serve as electrodes, and are connected to the secondary 18 of a suitable transformer, the primary winding 19 being connected to a power source 21 through a switch 20. A milliammeter 22 is included in the high voltage circuit. Backing films to be treated may be placed either on the bottom electrode as indicated at 23, or around the walls of the vessel as indicated at 24.

A strip of fused extruded polytetrafluoroethylene film 23 having a thickness of 0.004 inch was placed in the position indicated and the vessel evacuated to a pressure of 0.5 millimeter of mercury. Alternating current was supplied to the transformer at a voltage of up to about 600 volts, which dropped to about 500 volts during discharge and was just sufficient to cause a visible glow within the vessel, the current flowing in the system providing a measurement on the meter 22 of about 30 milliamperes. After thus exposing the film to u.v. light of wavelengths less than 2000 Angstroms for 60 seconds, the circuit was broken, air was admitted to the chamber, and the specimen was removed and tested.

The strip was applied to the adhesive surface of a section of pressure-sensitive adhesive tape and removed therefrom by stripping while measuring the removal effort required. When this test was applied to an untreated polytetrafluoroethylene film the force required was about 5 ounces for a width of 0.5 inch. The treated strip provided a removal effort under the same conditions of 37 ounces.

Fully equivalent results have been obtained by substituting continuous or pulsating direct current for alternating current in establishing the activating electrical discharge.

The surface resistivity of the treated film, while appearing to be somewhat lower than that of the untreated film, was greater than could be effectively measured by the usual methods employed in measuring high resistances, and was much greater than the surface resistivity of a polytetrafluoroethylene film which had been surface treated with metallic sodium in liquid ammonia and then carefully washed.

In another experiment the strip of polytetrafluoroethylene film, in this case having a thickness of 0.010 inch, was placed within the apparatus in the position indicated by the sample 24 in Figures 1 and 2. The vessel was evacuated, and voltage applied as before, in this instance for periods of 15 minutes and at a current of 200 milliamperes, providing a visible glow in each case. The pressure in the vessel was held at 75 microns, 250 microns, 500 microns, and 750 microns of mercury in a series of runs. The resulting treated film was in each instance coated with a thin layer of a heat-curing silicone pressure-sensitive adhesive composition which was subsequently cured by heating. Strips of the adhesive tape thus produced were then tested to determine the force necessary to separate the adhesive coating from the adhesive film surface. Under the conditions employed, a control sample of untreated film required a

force of 30 ounces per 0.5 inch width for adhesive removal, whereas the forces required for each of the four test specimens were 48, 52, 48, and 40 ounces per 0.5 inch, respectively.

Similar treatment and test was applied to a series of pigmented 0.002 inch polytetrafluoroethylene films. The films were treated under a pressure of 200 microns of mercury at a current input of 200 milliamperes for 16 seconds each, were coated with the heat-curing silicone pressure - sensitive adhesive composition which was then cured, and were tested for offsetting or removal of the adhesive layer. In this test, the 0.5 inch adhesive - coated film was adhered to a flat steel or other test panel and removed by stripping back over itself at constant speed. With the untreated films the film was found to come away from the adhesive coating at a force of between 12 and 20 ounces, whereas the adhesive coating applied to the treated film was not released at forces of up to 34 to 46 ounces, the force at which the coated film pulled away from the test surface. The treated film was not visibly distinguishable from the untreated.

Similar effects were obtained by treating polytetrafluoroethylene film in the apparatus of Figure 3. In this modification a copper conductor 25 is wound around the glass tube 10 of the apparatus of Figure 1. Specifically, a helical winding of 25 turns of No. 20 copper wire was used. The ends of the winding were connected to a variable condenser 26 and a source 27 of alternating potential, the constants of the circuit being selected to provide resonance at about 900 kilocycles thereby providing a visible glow within the evacuated chamber. A sample of polytetrafluoroethylene film 28 placed against the bottom member 11 as indicated in Figure 3, and exposed for 60 seconds to the discharge obtained under a vacuum of 0.5 millimeter of mercury, was tested on both exposed and protected surfaces by first applying a strip of pressure - sensitive adhesive tape and then measuring the force required to peel the tape from the surface. A force of 6 ounces removed the tape from the bottom or unexposed surface of the film, whereas a force of 21 ounces was required to remove the tape from the exposed top surface.

Figures 4 and 5 illustrate a semi - automatic treating chamber in which a glass tube 40, in this instance having an internal diameter of 8.375 inches, and closed at the ends by members 41 and 42 through gaskets 43 and 44, contains a pedestal platen 45 over which a strip of polytetrafluoroethylene or similar film 46 is drawn from a supply reel 47 to a windup reel 48. The film-carrying unit is surrounded by an open - centered metal plate 49. Both the plate 49 and the platen 45 are connected to the lower closure member 42 and serve as a lower electrode. The platen 45 is provided with an internal cooling means indicated by a tube 50; and the windup reel 48 is mechanically driven, by means not shown, so as to draw the film 46 over the platen 45 and through the activating zone at any desired speed.

A substantial yardage of 0.002 inch transparent polytetrafluoroethylene film several inches in width was activated at speeds providing exposures of 15 to 60 seconds under vacuum of a pressure of 0.5 millimeter of mercury and at a current input of 200 milliamperes which was sufficient to provide a visible glow within the evacuated chamber. The treated film was coated with a heat-curing silicone pressure - sensitive adhesive composition which was then cured, and the product was slit into desired widths and wound up in roll form to provide rolls of transparent pressure - sensitive adhesive tape. The tape could be unwound from roll form, applied to various surfaces under light finger pressure, and then removed therefrom, without splitting or offsetting of the adhesive layer. When a strip of this tape 0.5 inch in width was applied with its adhesive coating against a strongly adherent test surface and then pulled back lengthwise over itself, the film separated from the cured silicone adhesive at a force of about 70 to 75 ounces. With untreated polytetrafluoroethylene film tested in the same way, a force of only 5 ounces was needed. Such pressure - sensitive adhesive tape products, made with the untreated film, cannot successfully be unwound from roll form or removed from surfaces to which applied without an offsetting of adhesive.

Activation of polytetrafluoroethylene film was successfully accomplished in the apparatus just described at speeds up to 12 yards per minute, giving an exposure to the activating discharge of about 2 seconds.

The apparatus of Figures 6 and 7 consists of a heavy walled glass tube 60 in the form of a T, provided with gasketed end members 61, 62 and 63, vacuum connections 64 and 65, and an interior metal disc 66 having a central circular fluorite disc window 67. The end members 61 and 62 are connected to a source of high voltage alternating potential here indicated by a transformer 68.

A sample 69 of polytetrafluoroethylene film was placed over a fluorite window 67 as indicated in the drawing, and the system was evacuated on both sides of the disc 66 to a pressure of 0.5 millimeter of mercury. A potential was applied across the electrodes 61 and 62 for 2 minutes and at a value sufficient to provide within the tube a visible glow. The film sample was removed and was found to be hydrophilic over the area which had been in contact with the fluorite window while remaining hydrophobic on all other surface areas. Subsequent exposures in the same apparatus provided effective activation of poly-

tetrafluoroethylene or similar normally passive surfaces only when the fluorite window was first carefully cleaned by mild abrasive action.

The hydrophilic nature of the film surface treated as just described is an effective indication that the treated surface is active toward organic adhesives.

Much larger lengths of polytetrafluoroethylene film and the like have been treated in an apparatus such as indicated in Figure 8, in which the film 80 is drawn from a supply reel 81 to a windup reel 82 between two opposing electrode systems each consisting of a plate electrode 83 and a grid electrode 84. The plate electrodes are preferably provided with a cooling means, here indicated by a tube system 85. The entire assembly is contained within a tank 86 having a detachable cover 87 and connected to vacuum through an outlet 88, the interior pressure being measured on a vacuum gauge 89. The various electrodes are connected to external electrical supply systems through insulated leads as indicated in the drawing.

Auxiliary equipment is provided for driving the windup reel 82, maintaining tension on the stock reel 81, holding the two reels in proper alignment, determining the condition of the activating discharge, and the like. For example, inspection ports enable the operator to maintain a sustained visible glow between the operating plate and grid electrodes without sparking, as the film is drawn at a uniform rate past the electrode area.

It will be seen that the film 80 may be subjected to an activating discharge through a grid electrode and at either or both surfaces as it is drawn past the electrode systems within the evacuated chamber.

Polytetrafluoroethylene film was treated in the apparatus just described under a variety of conditions as to vacuum, time of irradiating and intensity of irradiation, comparable to those of the previous examples, and fully equivalent results in terms of surface activation were obtained.

Each of the preceding examples has involved treatment of the fluorocarbon polymer surface at reduced pressure by means of an electrical discharge producing a visible glow within an evacuated space and in direct line with the surface treated. It is believed that the activation is caused, at least in part, by impingement of ultraviolet rays of short wave length, that is, below 2000 Angstroms, on the surface of the polymer in the presence of oxygen. Since oxygen readily absorbs such rays, it might be expected that irradiation under reduced pressure would be essential. Surprisingly, it has been found that effective action may also be obtained at atmospheric pressure.

In one example, schematically represented in Figure 9, the surface of a section of polytetrafluoroethylene film 90 was subjected to the discharge from a pointed probe 91 supplied from a Tesla - coil source 92. The visible brush discharge from the point 91 covered an area of about one square inch with the point about 0.25 inch from the surface. The point was moved uniformly over the surface to cover a total of 8 square inches in about 15 seconds. The surface thus treated was coated with a heat-curing silicone pressure - sensitive adhesive composition which was then cured. A 0.5 inch wide strip of high strength commercial pressure - sensitive adhesive tape was pressed over the coated surface and was then stripped away at an angle of 180 degrees, thus removing the silicone adhesive from the corresponding area of the treated film. The force required for removal was 30 ounces. The force required in a control test on an untreated film was only 15 ounces.

The apparatus of Figure 10 consists of two flat plate metal electrodes 100 and 101 connected across a source of potential here indicated by a transformer 102, separated by thin glass plates 103 and 104 which in turn are separated by insulating spacers 105 and 106, forming an open space between the glass plates. A sample of polytetrafluoroethylene film 107 placed on the lower plate 104 is thus subjected to an intense electrical field, sufficient to provide a faint visible glow in the open space above the film.

In a specific example, a 2 by 4 inch segment of 0.002 inch polytetrafluoroethylene film was placed between glass plates each 3 millimeters in thickness, separated by 0.125 inch hard rubber spacers, and subjected to a potential of 12,000 volts at a current flow of 23 milliamperes. Full activation was obtained within 15 seconds. Prolonged treatment of up to 30 minutes did not alter the surface characteristics but in some instances caused further dielectric weakening of the film at areas of initial non-uniformity or other weakness. The treated film was compared with an untreated control sample for adherence of in situ cured silicone pressure - sensitive adhesive, by methods just described. The observed removal effort for 0.5 inch width strips of film was 16 to 18 ounces for the untreated film and 26 to 30 ounces for the treated film.

The activated surface of polytetrafluoroethylene and similar normally passive fluorocarbon - surfaced polymers is substantially unchanged in appearance from the original passive surface, even though significantly altered in its activity toward both aqueous and non-aqueous liquids and plastic masses. The activation perseveres even after contact with strong reagents and solvents. For example, washing the activated surface of a polytetrafluoroethylene film with solvents such as aliphatic and aromatic hydrocarbons and ketones, or with strong aqueous acids or alkalis, has been found to cause no significant diminution in the ability of such surfaces to be wet by,

or to retain, organic adhesive materials applied thereto.

All types of normally passive fluorocarbon surface materials, including, for example, films of polytetrafluoroethylene or of copolymers of tetrafluoroethylene and hexafluoropropylene formed by skiving from massive sintered cylinders as well as fused extruded films of this material, and polytrifluoromonochloroethylene, may be treated in the manner described above for the production of adhesive tapes.

The invention is useful for the preparation of insulating pressure - sensitive adhesive tape products, as has been shown above, and is particularly useful for the preparation of high temperature tapes employing silicone pressure - sensitive adhesives. Other types of adhesive may however be applied to the fluorocarbon film backings to produce useful adhesive tapes. For example pressure - sensitive adhesives based on acrylic acid ester polymers, as well as non - pressure - sensitive adhesives have been successfully applied. In demonstrating this type of adhesion, thin polytetrafluoroethylene films have been activated in a manner such as that described above and then bonded to thin aluminium panels by means of an intervening thin heat-curing layer of 100 parts of liquid epoxy resin and 10 parts of diethylene triamine curing agent. After curing the resin, the thin polytetrafluoroethylene film is found to be so firmly bonded thereto that it cannot be stripped from the panel without severe distortion. Effective bonding has also been obtained with heat-cured phenol-aldehyde resins. Under the same set of conditions, an untreated polytetrafluoroethylene film can be easily lifted from the cured resin surface without any distortion whatever.

There has thus been provided a method of producing adhesive tapes having backings in the form of films of highly fluorinated fluorocarbon polymers, such as polytetrafluoroethylene, which have surfaces which are normally passive toward organic adhesive materials. The method requires no chemical treatment and produces no visible change in the product and no weakening of the physical qualities of the product. There is produced a new product, namely an adhesive tape having a fluorocarbon polymer backing film which is capable of withstanding thermal, physical, chemical, and electrical stresses to substantially the same degree as fluorocarbon polymer films which have not been activated, but which in addition retentively accepts the applied adhesive.

WHAT WE CLAIM IS:—

1. A method of producing an adhesive tape comprising activating a surface of a backing in the form of a film of a passive hydrogen-free fluorocarbon by irradiating it with ultraviolet radiation of wave lengths less than 2000 Angstroms in the presence of at least trace amounts of oxygen and applying an organic adhesive to the activated surface.

2. A method according to claim 1 in which the backing is a film of polytetrafluoroethylene.

3. A method according to claim 1 or claim 2 in which a high voltage electrical discharge is used to evolve the short wave ultraviolet radiation.

4. A method of producing an adhesive tape according to any preceding claim substantially as described with reference to the accompanying drawings.

5. An adhesive tape produced by the method of any preceding claim.

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868463 1 SHEET

AMENDED SPECIFICATION

This drawing is a reproduction of the Original on a reduced scale

FIG. 1.

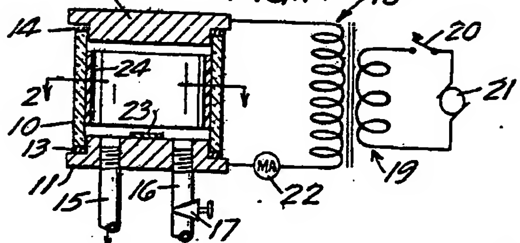

FIG. 2

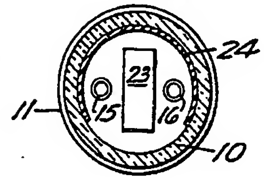

FIG. 3

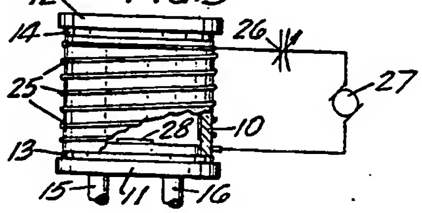

FIG. 4

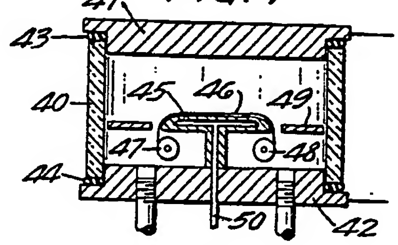

FIG. 6

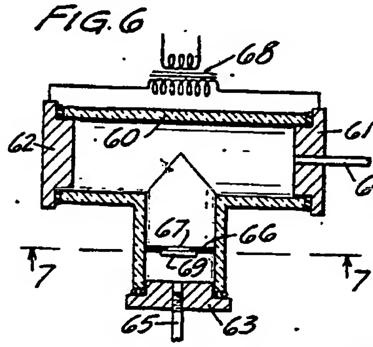

FIG. 5

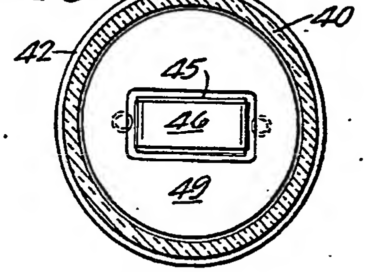

FIG. 7

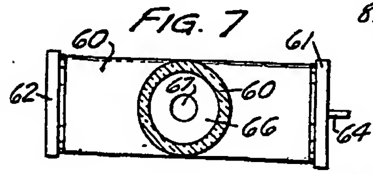

FIG. 8

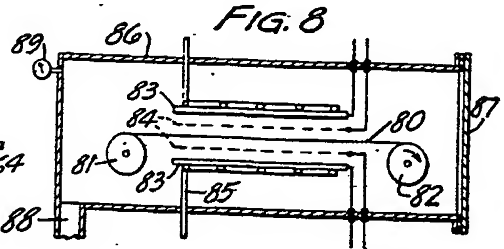

FIG. 10

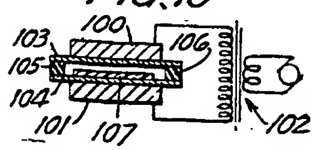

FIG. 9